Identification of a Discrete Peroxide Dianion, O_2^{2-} , in a Two Sodium-(1,6-Anhydro- β -maltose)₂-Peroxide Complex

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A complex formed by two 1,6-anhydro- β -maltoses with peroxide and two sodium ions has been isolated and determined to be [Na₂(1,6-anhydro- β -maltose)₂(H₂O)₃]O₂ by X-ray crystallography. The O₂ moiety, 1.496(2) Å for the O–O distances in the complex was identified as a discrete peroxide dianion, whereas two sodium and two carbohydrate molecules constitute a binuclear complex counter cation. The complex containing the discrete peroxide dianion was proven to be a useful oxidizing agent, which successfully oxidized α , β -unsaturated ketone to epoxyketone.

During our work¹ to study the specific complex formation of 1,6-anhydro sugar² prepared from corresponding free sugar through intramolecular dehydration, a complex of 1,6-anhydro- β -maltose (1) with sodium ion was obtained under alkaline conditions. The complex was identified as a 1:1 ratio of anhydro sugar with sodium ion by ion chromatography and elementary analysis. The repeated crystallization of the 1,6-anhydro- β -maltose–sodium complex under alkaline conditions afforded only a small amount of single crystals, whose structure was suggested to be [Na₂(1,6-anhydro- β -maltose)₂(H₂O)₃]O₂ (2) by initial X-ray crystallographic analysis. The peroxide complex might be afforded from accidental oxidation, and the O₂ moiety in the complex must be present as the peroxide dianion in order to maintain the charge balance. The dianion is immobilized within the complex crystal.

The peroxide dianion has been generally reported for organometallic peroxides recently. A heterocyclic organogallium peroxide has been synthesized, and the peroxo ligand with a O-O distance of 1.481 Å in the complex was identified as peroxide dianion.³ Such a situation with a dioxygen ligand coordinated by two metal atoms is well argued for transitionmetal compounds including proteins.⁴ The peroxide dianion was reported for lithium peroxo bicyclic guanidines and lithiated guanidinate,⁵ and the O-O distances in the complexes (1.501 and 1.505 Å) are suggested to be approaching the accepted value of 1.49 Å for purely ionic group 1 peroxides.⁶ Since a chracteristic feature of the peroxide with the O-O distance of 1.496(2) Å in the complex 2 is suggested to be purely ionic when compared with those in organometallic peroxides, the reproducible generation of the complex was conducted by the use of sodium peroxide. An aqueous solution of 1,6-anhydro- β maltose (1) was mixed with an equivalent amount of solid Na₂O₂, and then 2-propanol was gradually added to the resulting solution. Although a considerable loss of oxygen was observed when solid Na₂O₂ was dissolved in water, single crystals of 2 were deposited with up to 33% yield from 1. For the peroxide, 33% of O2 in parent Na2O2 was immobilized within the complex crystals 2.7 The reproducible generation of 2 was observed even by the use of 30% aqueous hydrogen peroxide with sodium hydroxide. The yield of **2** from parent **1** achieved over 80% when excess hydrogen peroxide was used.⁸ The complex formation with **1** in the presence of Na shows an exclusive system to capture peroxide dianions and preserve them as intact dianions.

Crystal structure determination9 revealed a novel binuclear complex cation, $(1,6-anhydro-\beta-maltoses)_2Na_2$, and an intact peroxide dianion, O_2^{2-} , becoming immobilized within the hydrogen-bond networks between two binuclear complexes (Figure 1). The peroxo group, 3.96–4.05 Å away from sodium ions, and the O-O bond and the line of Na-Na are perpendicular to each other. The sodium ions are seven-coordinated in a pentagonal bipyramid with seven Na+...O distances ranging 2.31 to 2.68 Å. Four of these Na⁺...O bonds are from one 1,6anhydro- β -maltose (1), including the glycosidic oxygen atom, and two are from another anhydro sugar molecule (Figure 2). This coordination sphere of Na is similar with that of [Na(18crown-6)H₂O]SCN. For 1,6-anhydro sugar 1, it provides O-2', -1', 5, 2 as a triethylene glycol array to coordinate with one Na⁺ and O-3', -2' as a ethylene glycol array to coordinated with another Na⁺, thus O-2' is shared for the coordination around both sodium ions (Figure 1). Remaining one Na+...O bond is from the water molecule, which is shared by two pentagonal bipyramids and completes the binuclear complex. Such a structure is provided as a result of the complex formation with the peroxide dianion. The O-O (1.49 Å) distance in the complex is exclusively adapted with the accepted value for the pure ionic peroxide.⁶ The peroxide dianion is surrounded by six hydroxy groups, three for each oxygen, from four carbohydrate molecules with six O_2^{2-} ...(H)O distances ranging 2.47 to 2.57 Å (Figure 3).

Two of these O_2^{2-} ...(H)O bonds are from the binuclear complex counter cation, and four are from two adjacent binuclear



Figure 1. Structure of the $[Na_2(1,6-anhydro-\beta-maltose)_2-(H_2O)_3]O_2$.



Figure 2. Na–O distances for $[Na_2(1,6-anhydro-\beta-maltose)_2-(H_2O)_3]O_2$.



Figure 3. Coordinatin around peroxide danion.

complexes. This shows the coordination sphere of the peroxide dianion is completed by hydrogen bonds to hydroxy groups of 1. The peroxide ion surrounded by water molecules is documented in the text, where Na₂O₂•8H₂O contains discrete peroxide ions to which the water molecules are hydrogen-bonded.⁶ The discrete peroxide dianion in 2 might be formed by the insertion of a hydroxy group from 1 into O⁻...Na⁺ ionic bond of Na₂O₂. The peroxide complex 2 was tested as an oxidizing agent for the epoxidation of α,β -unsaturated ketone¹⁰ and compared to the reaction using the parent sodium peroxide (Table 1). Although only a slight evolution of oxygen was observed when 2 was dissolved in water, the reaction using an equivalent amount of 2 afforded isophorone oxide as a sole product in good yield. On the other hand, the reaction with sodium peroxide suffered serious loss of oxygen, and the incomplete epoxydation with recovery of starting α,β -unsaturated ketone were observed. In the reaction, initially formed isophorone was gradually converted to 2-methoxyisophorone¹¹ via the epoxide ring opening with methoxide and elimination. For the reaction with hydrogen peroxide, the use of excess amount of H2O2 and catalytic amount of NaOH as standard condition¹⁰ is required to complete the epoxydation of isophorone. As a result, the peroxide complex 2 showed its efficiency as oxidizing agent for the epoxydation of α,β -unsaturated ketone.

In conclusion, we have demonstrated that the peroxide dianion is incorporated within the complex formation of 1,6-anhydro- β -maltoses and sodium counter cations. In the complex, the hydroxy groups of the carbohydrate moiety are hydrogen-

Table 1. The reactions were conducted in aq methanol at rt for 20 h based on the standaed condition¹⁰

$H_{3C} \xrightarrow{O_{1}} CH_{3} \xrightarrow{O_{2}} H_{3C} \xrightarrow{O_{2}} CH_{3} \xrightarrow{O_{2}} H_{3C} \xrightarrow{O_{2}} CH_{3} \xrightarrow{O_{2}} H_{3C} \xrightarrow{O_{2}} CH_{3}$				
Ovidizing	Molar	Yield (%)		Decovery
agent	ratio	Isophorone	2-Methoxy	(%)
agent	Tatio	oxide	isophorone	(70)
2	1	77	_	
Na_2O_2	1	13	17	25
$H_2O_2/NaOH$	1/1	23	48	
	1/0.17	65	5	13
	3/0.56	80	_	_

bonded to the peroxide dianion and retained it as the intact dianion. Such a novel immobilization of the peroxide dianion is due to the excellent complex formation ability of 1,6-anhydro- β -maltose with sodium ion. The characteristic feature of 1,6-anhydro disaccharide structures with the glycosyl moiety of 1C conformation provided the triethyleneglycol framework, which lead to capture sodium ion. The peroxide complex **2** successfully applied for the epoxidation of α , β -unsaturated ketone, and further application as the reagent is under investigation.

References and Notes

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- 7 Preparation of **2**. From Na_2O_2 : To a solution of **1** in water was added solid Na_2O_2 (1.0 mol equiv). After Na_2O_2 was dissolved, IPA was slowly added on the surface of the solution. **2** was deposited as single crystals (33% yield).
- 8 From H₂O₂: Using 1, NaOH (1.0 mol equiv) in water and 30% H₂O₂ (5 mol equiv), 2 was obtained (82%).
- 9 Crystal data for **2**: $C_{12}H_{23}O_{12.5}Na$, monoclinic, space group $P2_1$, a = 773.2(2), b = 2653.3(7), c = 790.8(3) pm, $\beta = 90.384(14)$, V = 1.6224(8) nm³, T = 123 K, Z = 4, $D_{calcd} = 1.598$ g cm⁻³, 19208 total reflections ($R_{int} = 0.024$), 9437 unique, $R(I > 2\theta(I)) = 0.0283$, $wR_2(I > 2\theta(I)) = 0.0838$. CCDC-756305.
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